Supporting Information: Structural Studies of Spray Pyrolysis Synthesized Oxygen Deficient Anatase TiO$_2$ Thin Films by using X-ray Absorption Spectroscopy.†

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Crystallite size of the thin films were calculated using Scherrer formula. The co-ordination number for the particular crystallites were calculated using the following equation:  

$$\frac{n_{\text{nano}}}{n_{\text{bulk}}} = \left[1 - \frac{3}{4} \frac{r}{R} \right] + \frac{1}{16} \frac{r}{R}$$

(1)

Table S1 represents the calculated co-ordination numbers considering the crystallite sizes of the films studied in the present manuscript. These nanometer sized crystallites ideally should have co-ordination number $\sim 5.9$. Hence, it can be concluded that the co-ordination number obtained (see Table 1 and 2 of the article) from the EXAFS analysis is due to oxygen deficiency obtained due to vacuum annealing. Presti et al. have calculated the cell parameters (a and c) and cell volume by using PAW, LCGTF and different potentials (Table S4 of Presti et al). The cell volume of ideal TiO$_2$ cell calculated by different methods were found out to be 144.3, 137.1, 138.2, 140.8 Å$^3$ and oxygen deficient TiO$_2$ cell were found out to be 144.0, 136.0, 138.1, 140.0 Å$^3$ by Presti et al. We have obtained cell volume $\sim 136.0$ Å$^3$ (see the last column of Table S1), which suggests the occurrence of oxygen vacancies in the cell.

1 Raman Studies of oxygen deficient TiO$_2$ thin films

The confirmation of anatase phase in pristine and annealed TiO$_2$ was studied by using Raman spectra. Raman spectra were recorded using 532 nm excitation with 50Âµobjective lens (numerical aperture of 0.8), 1800 gr.mm$^{-1}$ grating as monochromator and thermo electric cooled charged coupled device (CCD) as detector in a in-Via, Renishaw Raman Spectrometer.

Fig. S1 Raman spectra of pristine and annealed anatase TiO$_2$ synthesized at 450 °C.

Fig. S2 Raman spectra of pristine and annealed anatase TiO$_2$ synthesized at 500 °C.

Figure S1 and S2 represents the Raman spectra of pristine and annealed TiO$_2$ synthesized at 450 °C and 500 °C. The peaks at
Table S1 Crystallographic parameters and calculated co-ordination number.

<table>
<thead>
<tr>
<th>Sample id Crystallite Size (in nm)</th>
<th>Calculated Co-ordination number</th>
<th>Crystallographic cell parameter</th>
<th>Volume(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ 450 °C-2h 29</td>
<td>5.94</td>
<td>a=3.7842(2) c=9.4907(9)</td>
<td>135.9093(6)</td>
</tr>
<tr>
<td>TiO₂ 450 °C-4h 57</td>
<td>5.96</td>
<td>a=3.7801(0) c=9.5263(1)</td>
<td>136.1231(1)</td>
</tr>
<tr>
<td>TiO₂ 450 °C-6h 42</td>
<td>5.95</td>
<td>a=3.7827(4) c=9.4795(9)</td>
<td>135.6452(9)</td>
</tr>
<tr>
<td>TiO₂ 450 °C-8h 30</td>
<td>5.94</td>
<td>a=3.7794(2) c=9.4651(8)</td>
<td>135.0648(6)</td>
</tr>
<tr>
<td>TiO₂ 500 °C-2h 55</td>
<td>5.96</td>
<td>a=3.7775(1) c=9.4657(9)</td>
<td>135.0735(7)</td>
</tr>
<tr>
<td>TiO₂ 500 °C-4h 26</td>
<td>5.93</td>
<td>a=3.7789(3) c=9.4670(0)</td>
<td>135.1922(7)</td>
</tr>
<tr>
<td>TiO₂ 500 °C-6h 91</td>
<td>5.98</td>
<td>a=3.7806(3) c=9.5077(4)</td>
<td>135.8959(6)</td>
</tr>
<tr>
<td>TiO₂ 500 °C-8h 62</td>
<td>5.98</td>
<td>a=3.7809(7) c=9.5001(8)</td>
<td>135.8120(7)</td>
</tr>
</tbody>
</table>

144 cm⁻¹ (Eg), 394 cm⁻¹ (B₁g), 514 cm⁻¹ (A₁g) and 638 cm⁻¹ (Eg) peaks represent anatase TiO₂ phase. The presence of most prominent peak at 142.94 cm⁻¹ and less intense peak at 392.44 and 638.45 cm⁻¹ confirms the anatase phase in TiO₂ nanostructures for both the cases. Since, Si used as substrate, the 514 cm⁻¹ (A₁g) is merged with Si peak.

2 Delineating the presence of carbon dopant

A representative XAS spectrum from the data studied in this manuscript was considered to delineate the presence of carbon dopant. Ti-C path from a cubic space group f m-3m was considered for generation of Ti-C scattering path and it is at 2.16 Å. The position of this Ti-C path is shown in figure S3 along with the two Ti-O paths of anatase TiO₂ structure. Since the position of Ti-C path is at the first coordination shell, the fitting is done along with Ti-O paths. If TiC phase is present in the sample, weighted average of both Ti-O paths and Ti-C paths should fit the first coordination peak. We have taken the contribution of Ti-O paths as x and Ti-C path as 1-x. The initial value of x is taken as 0.5 with assumption of 50% contribution from each structure. The fitting results shows that the obtained x value is 0.9996, which clearly shows zero contribution of Ti-C path in the first coordination shell. The fitting contribution of Ti-C path and Ti-O paths in the first coordination shell is given in figure S4 of the supplementary information. In addition, X-ray absorption spectroscopy is inherently enabled to delineate between substitutional and interstitial position of the dopant, since it allows the iteration of the bond length during the fitting process. Moreover, TiC crystallises only in cubic phase and the peak of TiC path generated from the available crystal structure is at the first co-ordination sphere. Hence, it can be concluded that there is no carbon dopant in the TiO₂ films.
3 XAS Full Spectra and Imaginary $\chi(R)$ vs R plots.

![Graph](image)

**Fig. S5** X-ray absorption experimental curves for the oxygen deficient TiO$_2$ anatase films.

3.1 Correlation of peak height and peak position.

![Graph](image)

**Fig. S8** Plot of normalized height vs energy of the Ti pre-edge feature(A$_2$ peak)

A comparison of the above figure with the Figure 6 of ref[3] reveals that the samples considered in the present study contains both 5 and 6 co-ordinated Ti species.

**Notes and references**